Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: Effect of electrode materials

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ABSTRACT

This paper presents the removal of the antibiotic tetracycline (TeC) from water using electrochemical advanced oxidation processes (EAOPs); namely electrochemical oxidation (EO) and electro-Fenton (EF). The effect of different cathode materials (carbon-felt and stainless steel) on the direct/indirect electro-oxidation of tetracycline, and that of different anode materials (Ti/RuO_2–IrO_2, Pt and BDD) on both processes was systematically investigated for the first time. The EO process was found to be more efficient in using the carbon-felt cathode than the stainless steel cathode. The EO and the EF processes using BDD anode demonstrated superior oxidation/mineralization power. Almost total mineralization (TOC removal up to 98%) of $100\,mg\,L^{-1}$ TeC solutions was achieved after 6 h treatment either by EO and/or EF treatment with BDD anode. The oxidative degradation of TeC followed pseudo-first-order-reaction kinetics in using all tested electrodes and anode/cathode configurations. Apparent rate constants of different anode/cathode configurations increased in the following sequence: Ti/RuO_2–IrO_2/stainless steel < Ti/RuO_2–IrO_2/carbon-felt < BDD/carbon-felt (EO) < BDD/carbon-felt (EF). The electrical energy consumed per gram of TOC removal was calculated for different electrode configurations to assess the cost effectiveness of the EO and the EF processes to mineralize TeC in water.

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1. Introduction

In recent years, occurrence of pharmaceuticals in water is receiving increasing attention as emerging contaminants. The presence of pharmaceuticals in wastewater not only affects the water quality, but also causes long term potential adverse impacts on the ecosystems and the human health [1,2]. Among various pharmaceuticals, antibiotics are widely used in human and veterinary medicines to treat diseases and to promote growth [3]. Tetracycline (TeC) is one of the most commonly applied antibiotics and its production and usage rank second worldwide after antimicrobial sulfonamides [4–6]. Additionally, TeC merits attention because it has been extensively used to treat humans and account for more than 60% of total antibiotics used in animals for therapeutics [7]. TeC has been frequently detected in soil and water samples [8,9]. In soil samples, concentration of TeC ranged from 86 to 199 $\mu g\,kg^{-1}$ whereas detected concentrations of TeC residues in surface water

were at 0.07–1.34 $\mu g\,L^{-1}$. TeC in water may cause the spread of antibiotic resistant bacteria and antibiotic resistant genes in aquatic environment and thus constitutes a public health concern [10]. It is thus imperative to remove TeC from water adequately.

The physical removal methods such as adsorption, reverse osmosis or nanofiltration are able to separate TeC from water, but these methods only concentrate waste, without degradation, and induce another environmental problem [11]. Chemical oxidants like chlorine and chlorine dioxide have been applied to oxidize TeC [12], which form potential carcinogenic chlorinated byproducts. Ozonation, as advanced oxidation process (AOP), oxidizes TeC rapidly; however, incomplete mineralization was observed. Maximum removal of TOC was 40% after 2 h ozonation [4]. This weak mineralization degree was related to the relatively lower oxidation power of O_3 to mineralize reaction intermediates. Comparatively, electrochemical advanced oxidation processes (EAOPs) have shown much higher efficiency of mineralization and are the focus of the present study to mineralize TeC completely.

EOAPs have been widely investigated in recent years because of their low operating cost [13–17]. Electrochemical oxidation (EO) and electro-Fenton (EF) processes are two kinds of commonly used EAOPs based on in situ generation of highly oxidizing agent

hydroxyl radicals ($^\bullet$OH) ($E^\circ = 2.72$ V versus NHE). An EO process destroys the pollutant by the electro-generated $^\bullet$OH on a metallic (M) or metal oxide anode (reaction (1)) [18–20]. Heterogeneous $^\bullet$OH, formed at the anode surface, react efficiently with organics (reaction (2)) [21,22]. This process is highly potent in using a boron-doped diamond (BDD) anode, which has a high O_2 evolution overvoltage.

$$M + H_2O \rightarrow M(^\bullet OH) + H^+ + e^- \qquad (1)$$

$$M(^\bullet OH) + organics \rightarrow M + oxidation products \qquad (2)$$

In the EF process, homogeneous $^\bullet$OH are produced through the electrocatalytically generated Fenton's reagent ($H_2O_2 + Fe^{2+}$) in the bulk solution (reaction (3)) [14,23–25]. The regeneration of Fe^{2+} from Fe^{3+} takes place at the cathode (reaction (4)) [26–28], which subsequently regenerate $^\bullet$OH following the Fenton's reaction (reaction (3)).

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + {}^\bullet OH + H_2O \qquad (3)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$
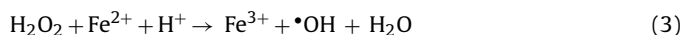
The oxidative degradation efficiency of the EF process depends on the nature of the cathode materials. For example, the carbon-felt (CF), which has large active surface and outstanding O_2 reduction performance, is an effective cathode material for electro-generating H_2O_2 in the reaction mixture (reaction (5)) [29].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (5)$$

This in situ production of H_2O_2 in combination with regeneration of Fe^{2+} allows continuous generation of $^\bullet$OH, based on reactions (3) and (4) [30].

Dimensionally stable anodes (DSA) [31,32], platinum (Pt) [33–36], and BDD [2,37,38,34,39] as anodes are commonly employed for treating organic pollutants [2,37,38,34,39]. Compared with DSA and Pt anodes, BDD is a relatively new anode material and has received greater attention since it has advantageous properties such as high oxygen overvoltage with extremely wide potential window, inert surface for adsorption, and strong oxidation power [40,41].

There are only handful studies reported on the application of AEOPs for the degradation of TeC [41–45]. To our knowledge, there has been no systematic study on the effect of different electrode materials on the electrochemical oxidation of TeC. Furthermore, no study on the degradation of TeC by the EF process has been reported previously.

Objectives of the present study are: (i) to investigate the effect of different cathode materials on the electrochemical oxidation of TeC, (ii) to learn the effect of different anode materials in both electrochemical oxidation and electro-Fenton processes on the oxidation of TeC, and (iii) to seek complete mineralization of TeC in water.

2. Materials and methods

2.1. Chemicals

Analytical grade (>98% purity) tetracycline hydrochloride, $C_{22}H_{24}N_2O_8 \cdot HCl$, was purchased from Fluka and was used in the electrolytic experiments without further purification. Sulfuric acid, anhydrous sodium sulfate, and ferrous sulfate heptahydrated of analytical grades, were purchased from Fluka and Acros Organics. All solutions were prepared with ultra-pure water obtained from a Millipore Mill-Q system with resistivity >18 MΩ cm at a room temperature.

2.2. Analytical procedures

The analysis of TeC was carried out by injecting 20 μL sample to the reversed-phase high performance liquid chromatography (HPLC) set-up, which had a Merck Lachrom liquid chromatograph, equipped with a L-7100 pump and was fitted with a Purospher RP-18, 5 μm, 25 cm × 4.6 mm (i.d.) column at 40 $^\circ$C. Detection was done using a L-7455 photodiode array detector and a selected wavelength was 280 nm. The concentration of TeC was determined periodically using an isocratic solvent mixture of water/methanol/acetic acid 24.5:74.5:1 (v/v/v) as a mobile phase at a flow rate of 0.8 mL min^{-1}.

The electrolyses were performed with a Hameg HM8040 triple power supply at a constant current. This instrument displayed the cell voltage along the treatments as well. The solution pH was measured by using a CyberScan pH 1500 pH-meter (Eutech Instruments). The mineralization of treated solutions was assessed from the abatement of their dissolved organic carbon, which can be considered as the total organic carbon (TOC) in the case of highly water-soluble organic compounds such as TeC. A Shimadzu VCSH TOC analyzer was used to determine TOC. Samples withdrawn from the treated solution at different electrolysis times were microfiltered onto a hydrophilic membrane (Millex-GV Millipore, pore size 0.22 μm) before subjected to analysis. Reproducible TOC values, within ±1% accuracy, were found using the non-purgeable organic carbon method.

2.3. Electrolytic systems for the degradation of TeC

For all the EAOPs, the electrolyses were performed in an open, undivided and cylindrical electrochemical cell of 6 cm diameter and 250 mL capacity in which the aqueous solutions of TeC were placed. Three electrodes, all with 24 cm^2 (4 cm × 6 cm) area were used as anode: commercial pure Pt, boron-doped diamond (BDD, thin-film deposited on a niobium substrate (CONDIAS, Germany), and commercial DSA (mixed metal oxide T_i/RuO_2–IrO_2) from Baoji Xinyu GuangJiDian Limited Liability Company, China). A stainless steel plate of 24 cm^2 (4 cm × 6 cm) area and a tridimensional, large surface area carbon-felt (14 cm × 5 cm × 0.5 cm in width, Carbone-Lorraine, France) electrodes were used as cathode.

In EF experiments, the anode was centered in the electrochemical cell and was surrounded by the cathode (case of carbon-felt), which covered with the inner wall of the cell. H_2O_2 was produced in situ from the reduction of dissolved O_2 in the solution. The concentration of O_2 in the solution was maintained by continuously bubbling compressed air through a frit at about 1 L min^{-1}. A period of 10 min before electrolysis was sufficient to reach a stationary O_2 level. Initial concentration of 0.1 mM Fe^{2+} as a catalyst in the electrolysis experiments was obtained by adding solid $FeSO_4 \cdot 7H_2O$ into the solution. The use of 0.1 mM Fe^{2+} is recommended as the catalyst optimum amount in the EF process with a minimum contribution of parasitic reactions [14,15]. A pH of 3.0 was considered as the optimum pH for the EF process.

The EO experiments were conducted either at a natural pH 4.3 of TeC solution or at pH 3.0, adjusted by adding H_2SO_4. In all cases, 220 mL synthetic aqueous solutions of 100 mg L^{-1} TeC containing 0.05 M Na_2SO_4 as a supporting electrolyte were subjected to electrolysis at room temperature (23 ± 2 $^\circ$C). A constant current of 200 mA was applied for kinetics studies while 500 mA current was applied for mineralization experiments. Solutions were vigorously stirred by a magnetic PTFE stirrer during the treatment to enhance the mass transport toward electrodes.
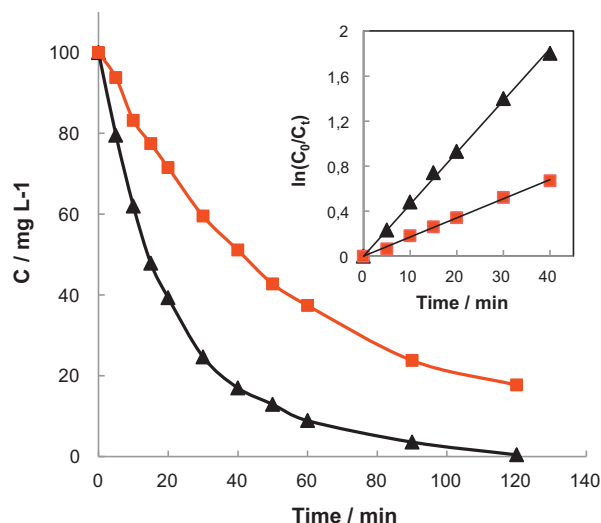
Fig. 1. Decay of the TeC concentration with reaction time for the electrochemical oxidation process using Ti/RuO$_2$–IrO$_2$ anode versus stainless steel (■) and carbon-felt (▲) cathodes at pH 4.3 and room temperature. The inset shows the kinetic analyses. Operating conditions: [TeC]$_0$ = 100 mg L^{-1} Na$_2$SO$_4$ = 0.05 M, I = 200 mA.

3. Results and discussion

3.1. Degradation of TeC by electrochemical oxidation with different cathode

The EO experiments were initially performed using the Ti/RuO$_2$–IrO$_2$ anode combined with carbon-felt (CF) and stainless steel (SS) cathodes. The initial concentration of TeC was 100 mg L^{-1} in 230 mL aqueous solution at pH 4.3. Results suggest that the Ti/RuO$_2$–IrO$_2$/CF cell was more efficient in oxidation of TeC than the Ti/RuO$_2$–IrO$_2$/SS cell (Fig. 1). The degradation of TeC followed apparent pseudo-first-order kinetics in both cells according to the following rate equation:

$$-\frac{dC}{dt} = kC \qquad (6)$$

where C is the concentration of TeC at time t and k is the pseudo-first-order rate constant. The values of k were calculated by plotting $\ln(C_0/C_t)$ versus t (Fig. 1 inset). Plots were linear and calculated values of k from the slopes are given in Table 1. In the case of Ti/RuO$_2$–IrO$_2$/SS cell, the value of k was approximately half the k determined in using Ti/RuO$_2$–IrO$_2$/CF cell (Table 1). The lower reactivity for the removal of TOC in the Ti/RuO$_2$–IrO$_2$/SS was also seen in the TOC values. Only 22% TOC removal in the Ti/RuO$_2$–IrO$_2$/SS cell (result not shown) was achieved at 6 h, under constant current electrolysis at 500 mA. The results show that this system was not sufficient to mineralize the cyclic oxidation intermediates of TeC and carboxylic acids formed during the oxidation of TeC C.

Overall, results of Fig. 1 indicate that the Ti/RuO$_2$–IrO$_2$ anode had weak oxidation/mineralization power in degrading organics. This is related to the lower oxidation power of the Ti/RuO$_2$–IrO$_2$ anode due to its relatively low O$_2$ evolution overpotential and chemisorption of the formed radicals. However, the amount of Ti/RuO$_2$–IrO($^\bullet$OH), produced in the cell Ti/RuO$_2$–IrO$_2$/SS (see reactions (1) and (2)), was sufficient to result in slow destruction of TeC.

Unlike the Ti/RuO$_2$–IrO$_2$/SS cell, the Ti/RuO$_2$–IrO$_2$/CF cell exhibited slightly better oxidation and mineralization efficiencies due to the continuous formation of H$_2$O$_2$ on the CF cathode that contributed to the oxidation of TeC. The effect of H$_2$O$_2$ alone on the oxidation of TeC was separately investigated by treating 100 mg L^{-1} solution with 0.2 and 1.0 mM H$_2$O$_2$. After 1 h reaction time, 5% and 17% TeC were oxidized for 0.2 and 1.0 mM H$_2$O$_2$ initial
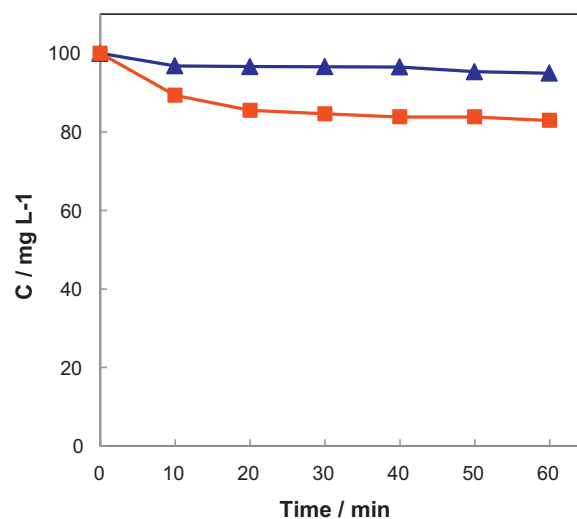

Fig. 2. Decay kinetics of 100 mg L^{-1} TeC C in aqueous medium with reaction time during its treatment with 0.2 (▲) and 2 (■) mM H$_2$O$_2$ at pH 4.3 (natural pH of tetracycline aqueous solution).

concentrations, respectively (Fig. 2). The results suggest that the direct oxidation rate of TeC by H$_2$O$_2$ was sluggish. Considering that the concentration of H$_2$O$_2$ produced by electrochemical reduction of O$_2$ on the CF cathode is far less than 0.2 mM, the contribution of H$_2$O$_2$ alone to TeC oxidation during EAOPs applied could be neglected under studied conditions. The better oxidation performance of the Ti/RuO$_2$–IrO$_2$/CF cell could be related to the electrochemical oxidation of H$_2$O$_2$ at the surface of the Ti/RuO$_2$–IrO$_2$ anode, which may lead to the formation hydroperoxy radicals (HO$_2$$^\bullet$) (reaction (7)) [14] that are significantly more powerful oxidant than H$_2$O$_2$.

$$H_2O_2 \rightarrow H^+ + HO_2^\bullet + e^- \qquad (7)$$

Therefore, subsequent experiments were conducted using the CF cathode. It should be pointed out that the oxidation power of the Ti/RuO$_2$–IrO$_2$/CF cell is better than that of Ti/RuO$_2$–IrO$_2$/SS cell, but the system remains insufficient to treat effectively organic pollutants due to requirement of more than 2 h for the complete oxidation of 100 mg L^{-1} TeC. Hence, different anode materials were tested in performing EO process.

3.2. Effect of anode materials on the degradation of TeC

The degradation of TeC by EO process using different anodes at different pH was investigated by keeping the same cathode as CF. First, the experiments were conducted at natural pH 4.3 of TeC solution. The tested anodes were Ti/RuO$_2$–IrO$_2$, Pt, and BDD. The influence of the anode material can be seen in Fig. 3. The time needed for total disappearance of 100 mg L^{-1} TeC in Ti/RuO$_2$–IrO$_2$/CF, Pt/CF, and BDD/CF cells at 200 mA constant current was 120, 60 and 40 min, respectively. The corresponding pseudo-first-order rate constants (k), calculated from the slope of $\ln(C_0/C_t)$ versus t plots (insert of Fig. 3), are given in Table 1. The BDD anode has a higher oxidation power and great ability to produce active radicals BDD($^\bullet$OH) than the Pt anode [14,38,46]. The Ti/RuO$_2$–IrO$_2$ anode had the lowest oxidation power among the three tested anode materials. The oxidation power of anodes was in agreement with the values of k (Table 1). This can be explained by the high amount of active BDD($^\bullet$OH) produced from the electrochemical oxidation of water by the BDD anode. Additionally, generated hydroxyl radicals are weakly adsorbed (physisorption) on the surface of BDD electrode, which allow them react in the

Table 1

Apparent (pseudo-first order) rate constants, k_{app} values for oxidation of TeC by hydroxyl radicals generated from different configuration of electrochemical advanced oxidation processes and TOC removal efficiency. $[TeC]_0 = 100\,mg\,L^{-1}$, $[Na_2SO_4] = 0.05\,M$, room temperature.

Electrochemical cell (anode/cathode configuration	Operating conditions	Apparent rate constants (min^{-1})	%TOC removal (at 6 h)
Electrochemical oxidation (natural TeC pH)			
Ti/RuO$_2$–IrO$_2$/SS[a]	$I = 200\,mA$	0.002	
Ti/RuO$_2$–IrO$_2$/CF[b]	pH = 4.3	0.046	
Pt/CF		0.098	
BDD/CF		**0.148**	
Electrochemical oxidation (pH set to 3)			
Ti/RuO$_2$–IrO$_2$/CF[b]	$I = 200\,mA$	0.037	
Pt/CF	pH = 3.0	0.037	
BDD/CF		**0.068**	
Electro-Fenton oxidation			
Ti/RuO$_2$–IrO$_2$/CF	$I = 200\,mA$	0.117	
Pt/CF	pH = 3.0	0.137	
BDD/CF		**0.182**	
Mineralization trials			
Ti/RuO$_2$–IrO$_2$/CF (**EF**)[c]	$I = 500\,mA$		22
Pt/CF (**EF**)	pH = 3.0		81
BDD/CF (**EF**)	$[Fe^{2+}] = 0.1\,mM$		**99**
BDD/CF (**EO**)[d] (without Fe^{2+})			**98**

Bold characters signify the optimal values.

[a] Stainless steel.
[b] Carbon-felt.
[c] Elecro-Fenton.
[d] Electrochemical oxidation.

reaction cage. Comparatively, hydroxyl radicals at the Pt anode are strongly adsorbed (chemisorption) on the surface and are therefore less mobile to perform oxidation of TeC.

Next, the degradation of TeC by EO process using different anodes was carried out at pH 3.0 by keeping other operating conditions similar to experiments at pH 4.3. The times needed for total disappearance of TeC in Ti/RuO$_2$–IrO$_2$/CF, Pt/CF, and BDD/CF cells were 150, 90 and 60 min, respectively (Fig. 4). The corresponding values of k_{app}, calulcated from the inset of Fig. 4, are given in Table 1. These results indicate that the oxidation kinetics of TeC C by hydroxyl radicals is slower at pH 3.0 compared to pH 4.3 for the three cells having different anodes. In fact, in contrast with EF process, there is no general view concerning the optimal pH in the EO process. Several works reported different pH as optimal value and the optimal pH depends usually on the target organic pollutant under study [14]. In the present study, oxidation of TeC at pH 4.3 (natural TeC solution pH) was better than that of pH 3.0. This suggests that the neutral molecular form of TeC (pH < pK_a = 3.3)

is less reactive with hydroxyls radicals than its anionic form at pH = 4.3 > pK_a. On the other hand, in the more potent cell configuration (BDD/CF cell), almost total mineralization (98%) could be reached in 6 h (see Fig. 6). A large amount of BDD($^\bullet$OH) was generated by the electrochemical oxidation of water, which can oxidize TeC rapidly and its aromatic/cyclic intermediates as well as short chain carboxylic acids, formed during the process. In addition, it is important to remark that at Pt anode, adsorption/desorption of by-products formed during TC should be considered.

3.3. Degradation of TeC by electro-Fenton process with different anodes

The effect of anode material on the degradation of TeC by the EF process was investigated by using Ti/RuO$_2$–IrO$_2$, Pt and BDD as anodes while CF was the cathode. Experiments were performed at pH 3.0, because it is the optimal pH to perform Fenton reaction and related processes as EF [47–49]. The time needed to completely
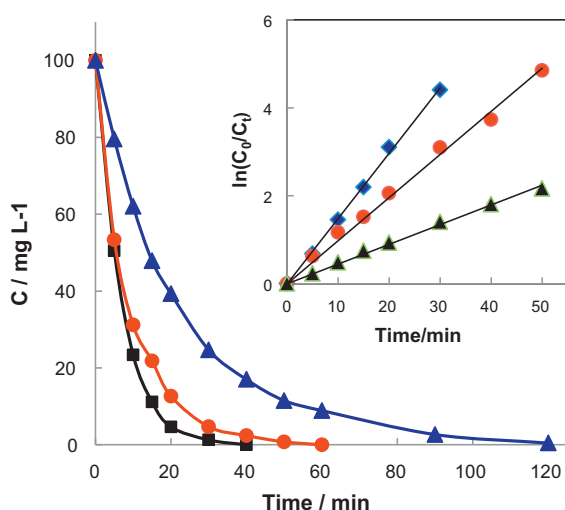

Fig. 3. Effect of the anode materials: Ti/RuO$_2$–IrO$_2$ (▲), Pt (●) and BDD (■) on the decay of the TeC concentration with reaction time during the electrochemical oxidation process. $[TeC]_0 = 100\,mg\,L^{-1}$, $[Na_2SO_4] = 50\,mM$, $I = 200\,mA$, pH 4.3. The insert shows the kinetics analyses.
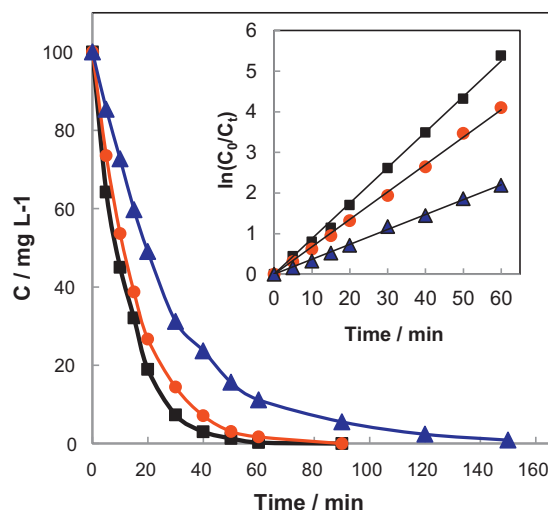

Fig. 4. Decay of the TeC concentration with reaction time for the electrochemical oxidation process with Ti/RuO$_2$–IrO$_2$ (▲), Pt (●) and BDD (■) anodes at constant current of $I = 200\,mA$, pH 3.0 and room temperature. The inset shows the kinetics analysis. Conditions: Cathode = carbon-felt, $[TeC]_0 = 100\,mg\,L^{-1}$, $[Na_2SO_4] = 0.05\,M$.
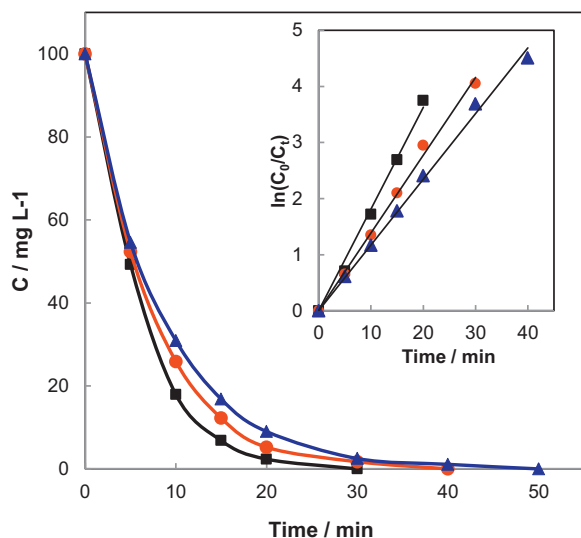
Fig. 5. Oxidative degradation kinetic curves during electro-Fenton treatment of 100 mg L^{-1}, TeC C with Ti/RuO$_2$–IrO$_2$) (▲), Pt (●) and BDD (■) anodes versus carbon-felt cathode at $I = 200$ mA constant current, pH 3.0 and room temperature in 0.05 M Na$_2$SO$_4$ in the presence of 0.1 mM Fe^{2+} as a catalyst.

Fig. 6. Evolution of solution TOC removal (as mineralization efficiency) as a function of treatment time in electrochemical oxidation process using: Ti/RuO$_2$–IrO$_2$/stainless steel (○), Pt/carbon-felt (♦) and BDD/carbon-felt (●) cells, and electro-Fenton process using Pt/carbon-felt (▲) and BDD/carbon-felt (■) cells. Operating conditions: Room temperature, [TeC]$_0$ = 100 mg L^{-1}, $I = 500$ mA, pH = 3.0, [Fe^{2+}] = 0.1 mM, [Na$_2$SO$_4$] = 0.05 M.

degrade TeC C were 50, 40 and 30 min, for Ti/RuO$_2$–IrO$_2$, Pt and BDD anodes, respectively (Fig. 5). The EF process also followed pseudo-first-order kinetics, and the corresponding pseudo-first-order (or apparent) constant (k) are given in Table 1. The order of the pseudo-first-order rate constants in using different anode materials in the EF process is in agreement with the order of the pseudo-first-order rate constants in the EO process. The results also indicate that the degradation rate in the EF process were higher than that in the EO process under each studied condition. This relationship could be described by the mode of hydroxyl radical production in the presence of TeC. In the EO process, hydroxyl radicals were only generated through the electrochemical oxidation of water (reaction (1)). The system is heterogeneous and generated M(•OH) could react with TeC C only at the anode surface. The oxidation reaction is thus limited by the surface area of the anode. Comparatively, the EF process involved both the electrogeneration of homogeneous •OH in the bulk solution (reactions (3)–(5)) and heterogeneous M(•OH) at the anode surface (reactions (1) and (2)). The EF process produced thus more hydroxyl radicals per unit time and TeC could be oxidized simultaneously by the homogeneous •OH in the bulk solution and by the heterogeneous M(•OH) at the anode surface. Consequently, the oxidative degradation efficiency was better in the EF process than the EO process.

TOC removal of a 100 mg L^{-1} TeC aqueous solution at pH 3.0 and 500 mA constant current was investigated by EF process using the CF cathode in order to assess the mineralization power of different cells. TOC removals percentages after 6 h treatment were 30, 80, and 99% for Ti/RuO$_2$–IrO$_2$/CF, Pt/CF and BDD/CF cells, respectively (Fig. 6). These results show that the efficiency of the classical EF process (Pt anode–CF cathode configuration) could be strongly enhanced by using a high O$_2$-overvoltage anode such as BDD instead of Pt one. In this case, hydroxyl radicals were simultaneously formed both in the bulk solution from homogeneous Fenton's reaction (reaction (3)) as well as at the BDD anode surface leading to a significant enhancement of their formation rate; causing the acceleration of the oxidation rate of organics (initial pollutants and oxidation intermediates) [38,50]. Moreover, almost complete mineralization (98%) could be reached in 6 h by the EO using BDD/CF cell. This is not surprising because the BDD(•OH) radicals can effectively mineralize short chain carboxylic acids, which are relatively recalcitrant to mineralization in the EF process. The
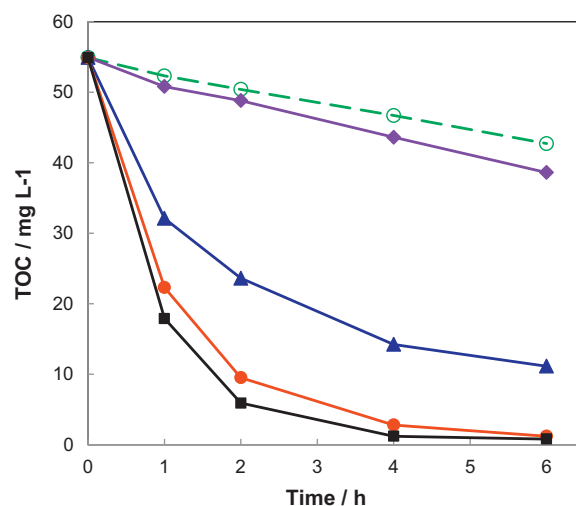
formation of Fe(III)–carboxylic acid complexes in EF process also decreases the mineralization efficiency of the process. Also, the mineralization of these complexes by homogeneous •OH becomes significantly less efficient at a longer period of time compared to the mineralization rate in the initial treatment time. In addition, it is well known that sulfat ion can be oxidized to peroxodisulfate ion at BDD anode and then contribute to the oxidation of CeT and its oxidation product to enhance the ovral efficiency of BDD/CF cell.

The electrical energy cost of the process relative to TOC removal at 6 h treatment time can constitute an interesting data. The amount of the electrical energy consumed (E, in kWh) per g TOC removed after completion of treatment was calculated using Eq. (8) and Fig. 6.

$$E = \frac{V \times I \times \Delta t}{\Delta(\text{TOC}) \times V_{\text{sol}}} \qquad (8)$$

where V (volt) is the potential between anode and cathode, I is the applied current (A), Δt is the treatment time (h), $\Delta(\text{TOC})$ is the amount of TOC removed (g carbon L^{-1}) and V_{sol} is the volume of the treated solution (L). Calculated values were 3.20, 1.10, and 1.30 kWh g^{-1} TOC for Ti/RuO$_2$–IrO$_2$–CF, Pt–CF and BDD–CF, respectively in the EF process. In the EO process, calculated value was 1.32 kWh g^{-1} for the BDD–CF. The calculated energy values suggest that the EF process using Ti/RuO$_2$–IrO$_2$ anode consumed three times more energy and also gave less efficient TOC removal performance under same operating conditions. It is interesting to note that the EF process with classical anode Pt consumed less electrical energy per unit TOC removal due to low cell potential related to its high conductivity. On the other hand, EF and EO processes using BDD anode had superior mineralization performances compared to the classical EF process with a Pt anode, and therefore seem to be more potent and suitable methods for mineralization of TeC aqueous solutions in particular, and for removal of organic pollutants from water, in general.

4. Conclusions

The degradation of TeC in both electrochemical oxidation and electro-Fenton process followed apparent pseudo-first-order reaction kinetics. The electrochemical oxidation experiments conducted by Ti/RuO$_2$–IrO$_2$ anode using different cathode indicate

that the Ti/RuO$_2$–IrO$_2$/CF cell was more efficient in TeC oxidation than the Ti/RuO$_2$–IrO$_2$–SS cell. The apparent (pseudo-first-order) rate constants of the oxidation of TeC by EO and EF processes with different anodes were found to follow the following order: Ti/RuO$_2$–IrO$_2$ < Pt < BDD. The oxidative degradation rate of TeC was better with different anodes at pH 4.3 (natural TeC solution pH) than that at pH 3 in the EO process. The degradation kinetics of TeC was faster in the EF process than the EO process. Both EO and EF processes with BDD anode and CF cathode showed outstanding mineralization ability. The removal of TOC was almost complete in both processes after 6 h treatment at 500 mA constant current electrolysis.

Acknowledgements

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